

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 495 375 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **92100179.8**

(51) Int. Cl.<sup>5</sup>: **C08F 4/74**

(22) Date of filing: **08.01.92**

(30) Priority: **16.01.91 US 642111**

(43) Date of publication of application:  
**22.07.92 Bulletin 92/30**

(64) Designated Contracting States:  
**AT BE DE ES FR GB IT NL**

(71) Applicant: **THE DOW CHEMICAL COMPANY**  
**2030 Dow Center Abbott Road**  
**Midland, MI 48640(US)**

(72) Inventor: **LaPointe, Robert E.**  
**3824 Todd Street**  
**Midland, Michigan 48640(US)**  
Inventor: **Rosen, Robert K.**  
**2612 Abbott Road 11**  
**Midland, Michigan 48642(US)**  
Inventor: **Nicklas, Peter N.**  
**4512 N. Saginaw Road 1120**  
**Midland, Michigan 48640(US)**

(74) Representative: **Sternagel, Hans-Günther, Dr.**  
**et al**  
**Patentanwälte Dr. Michael Hann, Dr. H.-G.**  
**Sternagel, Dr. H. Dörries, Sander Aue 30**  
**W-5060 Bergisch Gladbach 2(DE)**

(54) **Process for preparing addition polymerization catalysts via metal center oxidation.**

(57) **Addition polymerization catalysts comprising a derivative of a Group 4-8 metal compound prepared by metal center oxidation.**

**EP 0 495 375 A2**

This invention relates to a process for preparing certain catalytically active metal complexes. More particularly, this invention relates to such a process involving oxidation of the metal center of a complex to form active catalyst compositions useful for polymerizing olefins, diolefins and/or acetylenically unsaturated monomers.

5 The use of Ziegler-Natta type catalysts in the polymerization of addition polymerizable monomers is, of course, well known in the prior art. In general, these catalyst systems comprise a Group 4 or Lanthanide metal compound and a metal alkyl cocatalyst, particularly a trialkyl aluminum cocatalyst. Several preparations for homogeneous olefin polymerization catalysts are known. These involve reacting a transition metal chloride with a trialkyl aluminum compound, reacting a transition metal alkyl and a trialkyl aluminum  
10 compound, reacting a transition metal alkyl with a proton source, or reacting a transition metal alkyl with a molecular oxidant. In these examples the oxidation state of the transition metal remains unchanged or may actually be reduced.

In Polyhedron, 8(13-14), 1838-1843 (1989), M. Bochmann et al., disclosed an oxidative process for preparing bispentamethylcyclopentadienyltitanium methyl tetraphenylborate using silver tetraphenylborate oxidant in tetrahydrofuran solvent. The complex was inactive in the polymerization of ethylene.  
15

In J. Am. Ch. Soc. 109, 4111-4113 (1987) there is disclosed a process for preparation of cationic zirconium (IV) benzyl complexes by one electron molecular oxidation of d<sup>0</sup> organometallic compounds in tetrahydrofuran or methylene chloride solvent.

In both of the foregoing processes the solvents employed interfered with the resulting complex and detrimentally affected the catalytic ability of the catalyst in subsequent olefin polymerizations. In addition the references employed an oxidizing agent containing tetraphenylborate counter ion. Such anions, it has now been discovered, interfere with the resulting complex and are unacceptable for use in a metal center oxidation process for preparing addition polymerization catalysts.  
20

EP 416,815, published March 13, 1991 disclosed certain novel constrained geometry complexes possessing unique catalytic properties. EP 418,044, published March 20, 1991 discloses certain cationic constrained geometry catalysts that are particularly effective in polymerization of  $\alpha$  olefins. In pending United States Patent application S.N. 547,718, filed July 3, 1990, there is disclosed a unique oxidative activation procedure for preparing such complexes as are disclosed in EP 418,044 useful as addition polymerization catalysts.  
25

The present invention lies in the discovery of a novel technique for preparing the foregoing, cationic constrained geometry, metal complexes involving both metal center oxidation and cation complex formation in a single step. By combining what previously required two separate steps utilizing separate reagents and recovery systems, an improved and greatly simplified catalyst preparation is provided.  
30

In accordance with the present invention there is provided a process for the preparation of a catalyst useful for addition polymerizations corresponding to the formula:  
35

$L_1 MX_n^+ A^-$ , wherein:

L independently each occurrence is an anionic or nonanionic ligand or ligand system;

40 M is a metal of group 4-8 of the Periodic Table also having an oxidation state, M\*, one less than the state of the metal in the catalyst;

X independently each occurrence is hydride; halide; or a group selected from alkyl, alkenyl, silyl, germyl, aryl, and combinations thereof having up to 20 carbon, silicon or germanium atoms, and oxygen, halogen nitrogen, phosphorus and/or sulfur containing derivatives thereof;

45  $\ell$  is an integer greater than or equal to 1;

n is an integer greater than or equal to 1, and the sum of  $\ell$  and n together is one less than the valence of M; and

A<sup>-</sup> is a monovalent, compatible, noncoordinating anion,

the steps of the process comprising contacting under conditions to form the catalyst a reduced metal derivative corresponding to the formula:  $L_1 M^*X_n$ , wherein L,  $\ell$ , n, X, and M\* are as previously defined with an oxidizing agent capable of oxidizing M\* to form M and which in reduced form is noninterfering with the resulting catalyst, said oxidizing agent comprising a cationic oxidizer and a compatible noncoordinating anion, A<sup>-</sup>.  
50

Preferably the oxidizing agent corresponds to the formula:

55  $Ox^+ A^-$  (I)

wherein:

$Ox^+$  is a cationic oxidizer capable of oxidizing  $M^*$  to form  $M$ ; and

$A^-$  is a compatible noncoordinating anion.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

The term "anionic or nonanionic ligand or ligand system" refers to any ancillary, electron donating or electron sharing moiety. Such ligands include anionic ligands and neutral donor ligands.

Illustrative but nonlimiting examples of suitable anionic ligands include:  $R$ ,  $-R'(OR)_mOR$ ,  $(OR)_mOR$ ,  $-PR_2$ ,  $-SR$ ,  $-OR$ ,  $-NR_2$ , hydride, and organometalloid radicals comprising a Group 14 element wherein each of the hydrocarbyl substituents contained in the organic portion of said organometalloid, independently contains from 1 to 20 carbon atoms. In these ligands:

$R$  is a hydrocarbyl, silyl, germyl or a substituted hydrocarbyl, silyl, or germyl group of from 1 to 50 carbon, silicon, or germanium atoms;

$R'$  is  $C_{2-10}$  alkylene, and

$m$  is an integer from zero to ten.

Preferred anionic ligands are cyclopentadiene; substituted cyclopentadiene; biscyclopentadiene; and bridged biscyclopentadiene groups such as methylene or silane bridged biscyclopentadiene ligands. A most preferred anionic ligand is a substituted cyclopentadiene group more fully described hereafter.

Illustrative but non-limiting examples of suitable neutral donor ligands include:  $ROR$ ,  $NR_3$ ,  $PR_3$ , and  $SR_2$  wherein  $R$  is as above defined.

The term "cationic oxidizer" as used herein refers to an organic or inorganic ion having an oxidation potential sufficient to cause oxidation of the Group 4-8 metal center to the next higher oxidation state. Preferred cationic oxidizers have an oxidation potential of at least +0.20 volt and preferably at least +0.25 volt. Examples of suitable cationic oxidizers are ferrocenium and  $C_{1-4}$  alkyl substituted ferrocenium ions,  $Ag^+$ , triphenylmethyl cation, azoamines, ie.  $PhN=N(Ph)_2^+$ , wherein  $Ph$  is phenyl, etc.

As used herein, the recitation "compatible noncoordinating anion" means an anion which when functioning as a charge balancing anion in the catalyst system of this invention, does not transfer an anionic substituent or fragment thereof to any cationic species thereby forming a neutral metal product.

"Compatible anions" are anions which are not degraded to neutrality during catalyst preparation or use. Examples of compatible noncoordinating anions are provided hereafter.

The recitation "metalloid", as used herein, includes nonmetals such as boron, phosphorus which exhibit semi-metallic characteristics.

Preferred metals of Group 4-8 are titanium, zirconium, vanadium, chromium and iron. Especially preferred is titanium. Thus  $M$  is  $Ti(IV)$  and  $M^*$  is  $Ti(III)$ .

In the foregoing catalysts,  $X$  may include for example, hydride; halide (especially chloride); primary, secondary or tertiary alkyl; alkoxide; alkoxyalkyl; alkyl(polyalkyleneoxy)alkyl; dialkylaminoalkyl; dialkylaminoaralkyl; allyl; dialkylphosphinoalkyl; dialkylphosphinoaralkyl; etc. It has been found highly desirable when  $L$  is  $L'$ , as explained hereafter, that  $X$  should be capable of stabilizing the resulting complex. In such case  $X$  preferably is allyl or amino, phosphino or alkoxy substituted hydrocarbyl of up to 20 carbons.

Preferred reduced metal derivatives for use herein correspond to the formula:  $L'M^*X_n$ , wherein:

$L'$  is a divalent derivative of a substituted cyclopentadienyl group imparting a constrained geometry to the metal active site and containing up to 50 nonhydrogen atoms;

$M^*$  is as previously defined;

$X$  is a hydrocarbyl or an alkoxy, amino, phosphino or halo substituted hydrocarbyl group of up to 20 carbons; and

$n$  is one or two depending on the valence of  $M^*$ .

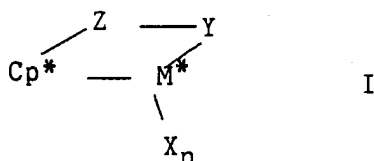
By use of the term "constrained geometry" herein is meant that the metal atom is forced to greater exposure of the active metal site because of one or more substituents on the cyclopentadienyl or substituted cyclopentadienyl group forming a portion of a ring structure wherein the metal is both bonded to an adjacent covalent moiety and is held in association with the cyclopentadienyl or substituted cyclopentadienyl group through an  $\eta^5$  bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is the metal may be symmetrically or unsymmetrically  $n$ -bound to the cyclopentadienyl or substituted cyclopentadienyl group.

The geometry of the active metal site is further defined as follows. The center of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective  $X$ ,  $Y$ , and  $Z$  coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The

angle,  $\theta$ , formed at the metal center between the center of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles,  $\theta$ , is less than in a similar, comparative complex differing only in the fact that the constraint-inducing substituent is replaced by hydrogen have constrained geometry for purposes of the present invention. Preferably one or more of the above angles,  $\theta$ , decrease by at least 5 percent more preferably 7.5 percent compared to the comparative complex. Highly preferably, the average value of all bond angles,  $\theta$ , is also less than in the comparative complex.

Preferably, monocyclopentadienyl metal coordination complexes according to the present invention have constrained geometry such that the smallest angle,  $\theta$ , is less than  $115^\circ$ , more preferably less than  $110^\circ$ , most preferably less than  $105^\circ$ .

Highly preferred reduced metal derivative compounds are monocyclopentadienyl titanium compounds corresponding to the formula:



wherein:

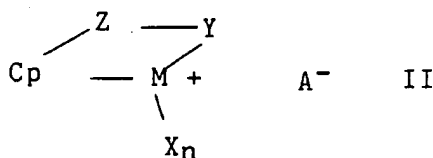
$\text{M}^*$ , X, and n are as previously defined;

$\text{Cp}^*$  is a cyclopentadienyl or substituted cyclopentadienyl group bound in an  $\eta^5$  bonding mode to  $\text{M}^*$ ;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; and

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

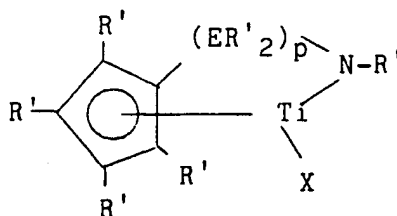
After metal center oxidation the catalysts correspond to the formula:



wherein Cp is a cyclopentadienyl or substituted cyclopentadienyl group bound in an  $\eta^5$  bonding mode to M, and, Z, M, X, n, and  $\text{A}^-$  are as previously defined.

Each of the four remaining carbon atoms in the cyclopentadienyl radical may be substituted or unsubstituted with the same or a different radical selected from the group consisting of hydrocarbyl radicals, substituted-hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, and halogen radicals. In addition two or more such substituents may together form a fused ring system. Suitable hydrocarbyl and substituted-hydrocarbyl radicals, which may be substituted for at least one hydrogen atom in the cyclopentadienyl radical, will contain from 1 to 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Suitable organometalloid radicals include mono-, di- and tri-substituted organometalloid radicals of Group 14 elements wherein each of the hydrocarbyl groups contain from 1 to 20 carbon atoms. More particularly, suitable organometalloid radicals include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, trimethylgermyl.

Most highly preferred reduced metal derivatives are amidosilane- or amidoalkanediy- compounds corresponding to the formula:



wherein:

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X is a hydrocarbyl or an alkoxy, amino, phosphino and/or halo substituted hydrocarbyl group of up to 20 carbons; and

p is 1 or 2.

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is methyl, ethyl, allyl, neopentyl, trimethylsilyl, norbornyl, benzyl, methylbenzyl, (dimethylamino)benzyl, (dimethylphosphino)benzyl, (diperfluorophenylamino)benzyl, phenyl, etc.

Specific preferred reduced metal compounds include: (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylamino)benzyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylamino)benzyl, (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (ethylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-methylene-titanium 2-(diperfluorophenylamino)benzyl, (tert-butylamido)dibenzyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanetitanium 2-(dimethylamino)benzyl, (benzylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanetitanium (dimethylaminomethyl)dimethylsilyl, (phenylphosphido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)-silanetitanium 2-(dimethylamino)benzyl.

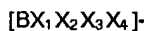
In the most preferred embodiment -Z-Y- is an amidosilane or amidoalkane group of up to 10 nonhydrogen atoms, ie. (tert-butylamido)(dimethylsilyl), (tert-butylamido)-1-ethane-2-yl, etc.

Other reduced metal derivatives which are useful in the process of this invention, especially compounds containing other Group 4-8 metals will, of course, be apparent to those skilled in the art.

Compounds useful as oxidizing agents in the preparation of the compounds of this invention preferably comprise a cationic oxidizer, and one or more compatible noncoordinating anions, as previously explained.

In a preferred embodiment A<sup>-</sup> of previous formula (I) comprises an anion which is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom, which anion is bulky and stable under the oxidation and subsequent polymerization conditions, and which anion is compatible with and noncoordinating towards the resulting Group 4-8 metal containing catalyst. The anion is employed only to provide charge balance without interfering with the oxidizing ability of Ox<sup>+</sup> or the catalytic properties of the resulting catalyst. Any metal or metalloid capable of forming a coordination complex which is stable under the reaction conditions of the present invention may be contained in the anion. Suitable metals include, but are not limited to, aluminum, gold, platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon. Oxidizing agents containing anions comprising a coordination complex containing a single boron atom are most preferred.

Anions comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein:

B is boron in a valence state of 3;

X<sub>1</sub> to X<sub>4</sub> are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon

or silicon atoms. In addition two or more of  $X_1$  to  $X_4$  may be linked to each other through a stable bridging group. Preferably  $X_1$  to  $X_4$  lack reactive hydrogen moieties. That is, the radicals are either devoid of hydrogen, contain only hydrogen in nonactivated positions or contain sufficient steric hindrance to protect potentially active hydrogen sites. Examples of preferred radicals for  $X_1$  to  $X_4$  are perfluorinated hydrocarbyl radicals containing from 1 to 20 carbon atoms. 3,4,5-trifluorophenyl, 3,5-di(trifluoromethyl)phenyl, etc. It has now been discovered that one of  $X_1$  to  $X_4$  may be a  $C_{1-10}$  organyl group, especially methyl or benzyl, without detrimentally affecting the inert properties of the anion.

A most highly preferred compatible, noncoordinating, anion is tetra(pentafluorophenyl)borate.

Suitable organic cationic oxidizers for use according to the present invention include ferrocenium ions, bis-indenyl Fe(III) ions, and cationic derivatives of substituted ferrocene, molecules, especially methyl substituted ferrocene. Suitable metal cationic oxidizers include  $Ag^+$ ,  $Pd^{+2}$ ,  $Pt^{+2}$ ,  $Hg^{+2}$ ,  $Hg_2^{+2}$ ,  $Au^+$  and  $Cu^+$ . Most preferred cationic oxidizers are ferrocenium, substituted ferrocenium, and  $Ag^+$  cations.

Illustrative, but not limiting, examples of oxidizing agents in the preparation of the improved catalysts of this invention are ferrocenium tetra(pentafluorophenyl)borate, 1,1'-dimethylferrocenium tetrakis(perfluorophenyl) borate, gold (I) tetrakis 3,4,5-trifluorophenyl borate, silver tetra(pentafluorophenyl)borate, 1,1'-dimethylferrocenium tetrakis 3,5-bistrifluoromethylphenyl borate.

Similar lists of suitable compounds containing other metals and metalloids which are useful as oxidizing agents (second components) could be made, but such lists are not deemed necessary to a complete disclosure. In this regard, it should be noted that the foregoing list is not intended to be exhaustive and other boron compounds that would be useful as well as useful compounds containing other metals or metalloids would be readily apparent, from the foregoing general equations, to those skilled in the art.

To recapitulate, it should be noted that the two compounds combined for preparation of the active catalyst must be selected so as to avoid transfer of a fragment of the anion, particularly an aryl group, to the metal cation, thereby forming a catalytically inactive species. This may be done by providing sufficient steric hindrance resulting from substituents on the groups attached to the Group 4-8 reduced metal derivative as well as substituents on the aromatic carbon atoms of the anion. It follows, then, that Group 4-8 reduced metal derivatives comprising perhydrocarbyl-substituted cyclopentadienyl radicals, for example, could be effectively used with a broader range of oxidizing agents than could reduced metal compounds comprising less bulky radicals. As the amount and size of the metal substituents are reduced, however, more effective catalysts are obtained with oxidizing agents containing anions which are more resistant to degradation, such as those with substituents on the meta and/or para positions of the phenyl rings. Another means of rendering the anion more resistant to degradation is afforded by fluorine substitution, especially perfluoro-substitution, in the anion. Oxidizing agents containing fluoro-substituted stabilizing anions may, then, be used with a broader range of first components. A preferred stabilizing anion is tetrakis(perfluorophenyl)borate.

In general, the catalyst can be prepared by combining the reduced metal derivative and oxidizing agent in a suitable noninterfering, noncoordinating solvent at a temperature from  $-100^\circ C$  to  $300^\circ C$ , and recovering the resulting product.

"Addition polymerizable monomers" usefully polymerized by catalysts prepared according to the process of the present invention include for example ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, polyenes, carbon monoxide, etc. Preferred monomers include the  $C_{2-10}$   $\alpha$ -olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene,  $C_{1-5}$  alkyl substituted styrene, tetrafluoroethylene, vinylbenzocyclobutane, ethylenenorbornene and 1,4-hexadiene.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, for example, temperatures from  $0$  to  $250^\circ C$  and pressures from atmospheric to 1000 atmospheres. Suspension, solution, slurry or gas phase process condition may be employed. A support may be employed but preferably the catalysts are used in a homogeneous manner. Hydrogen or similar chain terminator may be employed to control polymer molecular weight. It will, of course, be appreciated that the catalyst system will form *in situ* if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

Suitable solvents for the formation of the catalyst are noncoordinating, inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated  $C_{4-10}$  alkanes, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene.

Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, vinyltoluene (including all isomers alone or in admixture). Mixtures of the foregoing are also suitable.

It is believed that the active catalyst species of the present invention contains a metal center which remains cationic and has a metal-carbon bond which is reactive with olefins, diolefins and acetylenically unsaturated compounds. Also associated with this metal center are one or more charge balancing anionic remnants of the formula  $A^-$ .

The catalyst formed by the method of this invention may be retained in solution or separated from the solvent, isolated, and stored for subsequent use. As previously indicated supra, the catalyst may also be prepared *in situ* during a polymerization reaction by passing the separate components into the polymerization vessel where the components will contact and react to produce the improved catalyst of this invention.

The equivalent ratio of reduced metal derivative to oxidizing agent employed in the process is preferably in a range from 0.1:1 to 10:1, more preferably from 0.75:1 to 2:1, most preferably 1.0:1.0. In most polymerization reactions the equivalent ratio of catalyst:polymerizable compound employed is from  $10^{-12}$ :1 to  $10^{-1}$ :1, more preferably from  $10^{-8}$ :1 to  $10^{-5}$ :1.

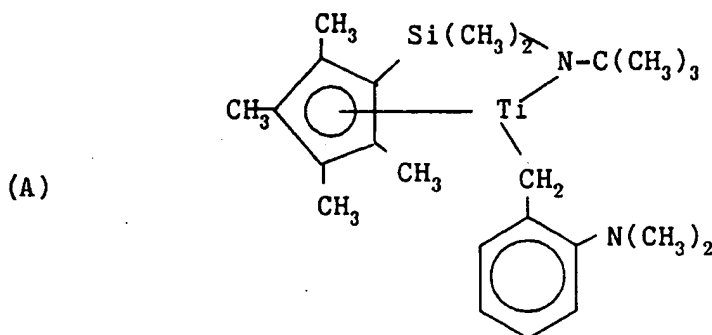
A beneficial feature of some of the catalysts of this invention, particularly those based on monocyclopentadienyl substituted titanium compounds in combination with an oxidizing agent comprising boron, is that when the catalysts of this invention are used to copolymerize  $\alpha$ -olefins, either alone or in combination with diolefins, the amount of higher molecular weight olefin or diolefin incorporated into the copolymer is significantly increased when compared to copolymers prepared with the more conventional Ziegler-Natta type catalysts. The relative rates of reaction of ethylene and higher  $\alpha$ -olefins with the aforementioned titanium-based catalysts of this invention are so similar that the monomer distribution in copolymers prepared with the catalysts of this invention may be controlled by the ratio of monomeric reactants. Certain of the catalysts are also useful to prepare polymers of vinylaromatic monomers having a high degree of syndiotacticity. Such catalysts have been previously disclosed in copending United States application Serial Number 559,475, filed July 30, 1990, and assigned to the same assignee as the present application.

In general, catalysts prepared by the present process produce polymer products which will be free of certain trace impurities generally found in polymers produced with Ziegler-Natta type catalysts such as aluminum, magnesium, chloride. The polymer products produced with the catalysts of this invention should, then, have a broader range of applications than polymers produced with more conventional Ziegler-Natta type catalysts comprising a metal alkyl such as an aluminum alkyl.

Having described the invention the following examples are provided as further illustration thereof and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis.

#### Example 1

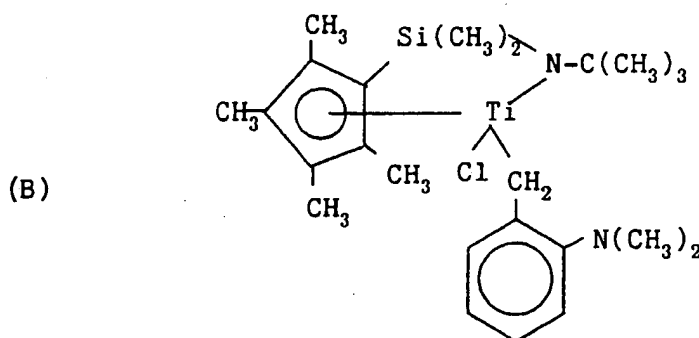
Preparation of reduced metal derivative (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanetitanium (III) (orthodimethylamino)benzyl,  $((CH_3)_4Si(CH_3)_2N-C(CH_3)_3)Ti(o-CH_2C_6H_4N(CH_3)_2)$  (formula A)



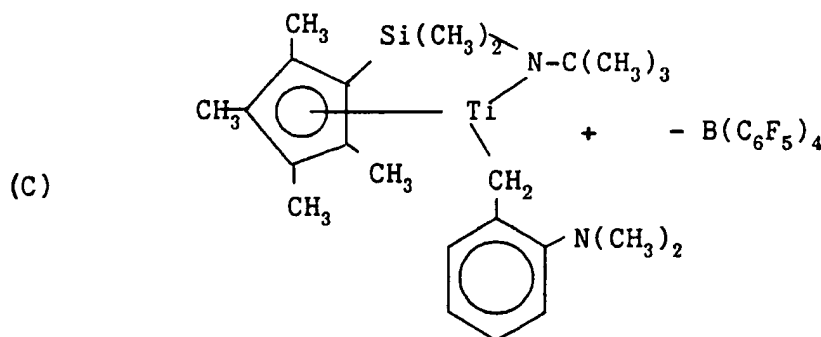
In the drybox, 0.25 g of  $TiCl_3(THF)_3$  and 0.35 g of  $(MgCl)_2((CH_3)_4Si(CH_3)_2N-C(CH_3)_3)(THF)_2$ , prepared according to the technique of EP 416,815 by reaction of (tert-butylamino)dimethyl-

(tetramethylcyclopentadienyl)silane with isopropylmagnesium chloride in a molar ratio of 1:2. The silane starting reactant was prepared by reacting dimethyldichloro silane with sodium 1,2,3,4-tetramethylcyclopentadienide at  $-40^{\circ}\text{C}$  in tetrahydrofuran solvent, followed by reaction of the r covered product with butylamine in tetrahydrofuran at  $25^{\circ}\text{C}$  for several hours were mixed at  $25^{\circ}\text{C}$ . 15 mL of tetrahydrofuran (THF) were added to give a purple solution. After 5 minutes, 95 mg of (o-dimethylamino)benzyl lithium, o-LiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>, prepared by reaction of n-butyl lithium with o-(dimethylamino)toluene in refluxing tetrahydrofuran in 5 mL of THF were added. After 30 minutes, the volatile materials were removed under reduced pressure to yield a red-brown solid. Pentane (20 mL) was added, the solution was filtered, and the volatile materials were removed to give a sticky red-brown solid. This solid was again dissolved in pentane, filtered, and cooled to  $-45^{\circ}\text{C}$ . Red crystals were isolated by filtration and dried. The electron paramagnetic resonance (EPR) spectrum of this material exhibited a single line at room temperature ( $g = 1.974$ ) and 2 lines at 77 K (consistent with a plane of symmetry in the molecule).

Proper identity of the reduced metal complex was confirmed by also preparing the Ti(IV) chloride of the above complex (Formula B) by reaction with lead (II) chloride and analyzing the NMR spectra.



Preparation of catalyst: (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane-titanium (IV) o-dimethylaminobenzyl tetrakis(perfluorophenyl)borate  $[(\text{CH}_3)_4\text{C}_5\text{Si}(\text{CH}_3)_2\text{N}-\text{C}(\text{CH}_3)_3\text{Ti}(\text{o}-\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)]-\text{B}(\text{C}_6\text{F}_5)_4$ -(Formula C)



A 50 ml flask was charged with 0.170g of  $[(\text{CH}_3)_4\text{C}_5\text{Si}(\text{CH}_3)_2\text{N}-\text{C}(\text{CH}_3)_3\text{Ti}(\text{o}-\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)]$  (0.463 mmol) and 25 ml of toluene. To the resulting red solution 0.280g (0.382 mmol) of ferrocenium tetrakis(perfluorophenyl) borate was added as a solid. The solution was stirred for one hour. After this time period the solvent was removed under reduced pressure to give a red oil. The resulting oil was triturated with pentane to give an orange solid. The solid was collected by filtration and washed with toluene (150 ml), dried under reduced pressure to give 0.289g (69 percent yield) of product.  $^1\text{H}$  NMR (thf- $d_8$ )  $\delta$  7.57-7.65 (m, 4H), 2.71 (s, 3H), 2.33 (bs, 3H), 2.21 (s, 3H), 0.84 (s, 9H), 0.71 (s, 6H).

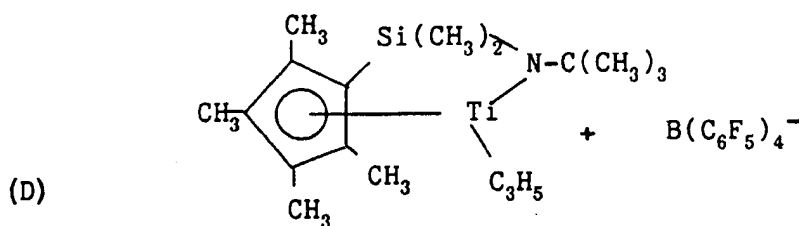
#### Example 2



Preparation of reduced metal derivative (tetrabutylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)-silanetitanium (III) allyl,  $((\text{CH}_3)_4\text{C}_5\text{Si}(\text{CH}_3)_2\text{N}-\text{C}(\text{CH}_3)_3)\text{Ti}(\text{C}_3\text{H}_5)$

In the drybox, 0.30 g of  $\text{TiCl}_3(\text{THF})_3$  and 0.42 g of  $(\text{MgCl})_2((\text{CH}_3)_4\text{C}_5\text{Si}(\text{CH}_3)_2\text{N}-\text{C}(\text{CH}_3)_3)(\text{THF})_2$  were mixed in a Schlenk tube. 20 mL of THF was added to give a purple solution. The Schlenk tube was sealed and removed to a Schlenk line, and the solution was cooled to  $-30^\circ\text{C}$ . 0.81 mL of 1.0 M allylmagnesium bromide was added by syringe. After 20 minutes, the solution was warmed to  $0^\circ\text{C}$  and the volatile materials were removed under reduced pressure to yield a dark solid. While keeping the flask at  $0^\circ\text{C}$  pentane (30 mL) was added, and the deep red solution was filtered, concentrated to ca. 5-7 mL, and cooled to  $-40^\circ\text{C}$ . Red crystals were isolated by filtration and dried in 22 percent yield. The EPR spectrum of this material exhibited a single line at room temperature and 2 lines at 77 K (consistent with a plane of symmetry in the molecule).

Preparation of catalyst: (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanetitanium (IV) allyl tetrakis(perfluorophenyl)borate  $((\text{CH}_3)_4\text{C}_5\text{Si}(\text{CH}_3)_2\text{N}-\text{C}(\text{CH}_3)_3)\text{Ti}(\text{C}_3\text{H}_5)] + \text{B}(\text{C}_6\text{F}_5)_4^-$  (Formula D)



The reaction conditions of Example 1 are substantially repeated using equal molar amounts of the above reduced metal derivative and ferrocenium tetrakis-perfluorophenyl borate as the anionic oxidizer to cause metal center oxidation.

#### Polymerizations

A 2 L stirred reactor was charged with the desired amounts of mixed alkane solvent (Isopar™ E, available from Exxon Inc.) and 1-octene comonomer. The reactor was heated to the polymerization temperature and saturated with ethylene at the desired pressure. Hydrogen chain terminator was added by differential pressure expansion from a ~75 mL addition tank. Catalyst were prepared in a drybox by syringing the desired amount of 0.0050 M reduced metal derivative solution (in toluene) into a suspension of the solid cationic oxidizer in toluene to provide equal molar ratios of reduced metal derivative and cationic oxidizer. This solution was then transferred to a catalyst addition tank and injected into the reactor. The polymerization was allowed to proceed for the desired time and the solution was removed from the reactor and quenched with hindered phenol anti-oxidant and isopropanol. The polymers were air-dried overnight and then dried in a vacuum oven.

A comparative example was provided utilizing the reduced metal derivative of Examples 1 but using a cationic oxidizer having a coordinating or interfering anion, tetraphenylborate. The comparative polymerization resulted in drastically reduced reaction yield.

Results are contained in Table I.

Table I

Run	Catalyst	Cat. Amt. μmole	Solvent (ml)	Comonomer (ml)	Ethylene KPa	Δ H <sub>2</sub> KPa	Temp. °C	Time (Min.)	Polymer (g)
1	Ex. 1	10	1000	200	3100	340	130	10	192.0
2	Ex. 1	2.5	1150	50	3400	70	150	10	57.8
3	Ex. 1	1	1100	100	3400	70	150	10	55.3
4	Ex. 2	10	1000	200	3100	340	130	10	73.5
5	Ex. 2	10	850	350	3100	170	90	15	228.4
*	1.	10	1000	200	3400	340	130	15	69.7

\*. comparative

1. (Me<sub>4</sub>C<sub>5</sub>SiMe<sub>2</sub>N-tert-Bu)Ti(o-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) and [(MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe]<sup>+</sup>[Ph<sub>4</sub>B]<sup>-</sup>

## 55 Claims

1. A process for the preparation of a catalyst useful for addition polymerizations corresponding to the formula:

$L_t MX_n^+ A^-$ , wherein:

L independently each occurrence is an anionic or nonanionic ligand or ligand system;

M is a metal of group 4-8 of the Periodic Table also having an oxidation state,  $M^*$ , one less than the state of the metal in the catalyst;

X independently each occurrence is hydride; halide; or a group selected from alkyl, alkenyl, silyl, germyl, aryl, and combinations thereof having up to 20 carbon, silicon or germanium atoms, and oxygen, halogen nitrogen, phosphorus and/or sulfur containing derivatives thereof;

t is an integer greater than or equal to 1;

n is an integer greater than or equal to 1, and the sum of t and n together is one less than the valence of M; and

$A^-$  is a monovalent, compatible, noncoordinating anion, the steps of the process comprising contacting under conditions to form the catalyst a reduced metal derivative corresponding to the formula:  $L_t M^*X_n$ , wherein L, t, n, X, and  $M^*$  are as previously defined with an oxidizing agent capable of oxidizing  $M^*$  to form M and which in reduced form is noninterfering with the resulting catalyst, said oxidizing agent comprising a cationic oxidizer and a compatible noncoordinating anion,  $A^-$ .

2. A process according to Claim 1 wherein the oxidizing agent corresponds to the formula:

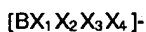


wherein:

$Ox^+$  is a cationic oxidizer capable of oxidizing  $M^*$  to form M; and

$A^-$  is a compatible noncoordinating anion.

3. A process according to Claim 2 wherein  $A^-$  is:



wherein:

B is boron in a valence state of 3,

$X_1$  to  $X_4$  are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms and optionally two or more of  $X_1$  to  $X_4$  may be linked to each other through a stable bridging group.

4. A process according to Claim 3 wherein  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$  are perfluorinated hydrocarbyl radicals containing from 1 to 20 carbons.

5. A process according to Claim 3 wherein  $Ox^{+a}$  is ferrocenium, inertly substituted ferrocenium, or  $Ag^{+1}$ .

6. A process according to Claim 1 wherein M is titanium.

7. A process according to Claim 1 wherein L is:

a) an anionic ligand selected from the group consisting of, R,  $-R'(OR')_mOR$ ,  $(OR')_mOR$ ,  $-PR_2$ ,  $-SR$ ,  $-OR$ ,  $-NR_2$ , hydride, and organometalloid radicals comprising a Group 14 element wherein each of the hydrocarbyl substituents contained in the organic portion of said organometalloid, independently, contains from 1 to 20 carbon atoms, wherein

R is a hydrocarbyl, silyl, germyl or a substituted hydrocarbyl, silyl, or germyl group of from 1 to 50 carbon, silicon, or germanium atoms;

R' is  $C_{2-10}$  alkylene, and

m is an integer from zero to ten; or

b) a neutral donor ligand selected from the group consisting of,  $ROR$ ,  $NR_3$ ,  $PR_3$ , and  $SR_2$  wherein R is as above defined.

8. A process according to Claim 7 wherein L is a divalent derivative of a substituted cyclopentadienyl group imparting a constrained geometry to the metal active site and containing up to 50 nonhydrogen atoms.

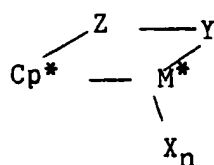
9. A process according to Claim 8 wherein L is -Cp\*-Z-Y- wherein

Cp\* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an  $\eta^5$  bonding mode to M\*;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

10. A process according to Claim 1 wherein  $L_1 M^* X_n$  corresponds to the formula:



wherein:

Cp\*, M\*, and n are as previously defined;

X is a hydrocarbyl or an alkoxy, amino, phosphino and/or halo substituted hydrocarbyl group of up to 20 carbons;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; and

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



11 Publication number:

**0 495 375 A3**

12

## EUROPEAN PATENT APPLICATION

21 Application number: **92100179.8**

51 Int. Cl.<sup>5</sup>: **C08F 4/74**

22 Date of filing: **08.01.92**

30 Priority: **16.01.91 US 642111**

43 Date of publication of application:  
**22.07.92 Bulletin 92/30**

64 Designated Contracting States:  
**AT BE DE ES FR GB IT NL**

88 Date of deferred publication of the search report:  
**19.11.92 Bulletin 92/47**

71 Applicant: **THE DOW CHEMICAL COMPANY**  
**2030 Dow Center, Abbott Road**  
**Midland, MI 48640(US)**

72 Inventor: **LaPointe, Robert E.**  
**3824 Todd Street**  
**Midland, Michigan 48640(US)**  
Inventor: **Rosen, Robert K.**  
**2612 Abbott Road 11**  
**Midland, Michigan 48642(US)**  
Inventor: **Nicklas, Peter N.**  
**4512 N. Saginaw Road 1120**  
**Midland, Michigan 48640(US)**

74 Representative: **Sternagel, Hans-Günther, Dr.**  
**et al**  
**Patentanwälte Dr. Michael Hann, Dr. H.-G.**  
**Sternagel, Dr. H. Dörries, Sander Aue 30**  
**W-5060 Bergisch Gladbach 2(DE)**

54 **Process for preparing addition polymerization catalysts via metal center oxidation.**

57 Addition polymerization catalysts comprising a derivative of a Group 4-8 metal compound prepared by metal center oxidation.

**EP 0 495 375 A3**



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 92 10 0179

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D, A	POLYHEDRON vol. 8, no. 13, 1989, pages 1838 - 1843; BOCHMAN M.: 'Synthesis of cationic alkyl bis(cyclopentadienyl)titanium complexes by one-electron oxidation of titanium(III) alkyls:' * the whole document * --- A EP-A-0 277 004 (EXXON CHEMICALS PATENTS INC.) * the whole document * -----	
		CLASSIFICATION OF THE APPLICATION (Int. Cl.5)  C08F4/74
		TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C08F
The present search report has been drawn up for all claims		
Place of search THE HAGUE	Date of completion of the search 11 SEPTEMBER 1992	Examiner FISCHER B. R.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document		